

MICROWAVE CURABLE COMPOSITIONS

FIELD OF THE INVENTION

5 The present invention relates to microwave curable compositions and to methods of controllably heating and curing heat curable compositions.

BRIEF DESCRIPTION OF RELATED TECHNOLOGY

10 Conventional techniques of heat curing compositions include the use of hot air, hot press and radiant heat. The equipment currently needed to perform these curing methods has safety and cost concerns. Such equipment also uses a great deal of energy in operation, in the form of heat which does not assist in curing the material. Such equipment is usually bulky, taking up costly manufacturing space and requires a great deal of maintenance and safety attention. These heating curing methods can be time consuming, especially when thick sections are cured and it takes a long time for the heat to transfer throughout the polymeric composition. Also, 15 these methods may cure sections of a thick article unevenly, leaving sections uncured and degrading other sections.

20 Microwave energy is a heating means that advantageously increases the speed and lowers the power consumption of heating an article. However, use of microwave energy has been limited as a heating means for polymeric compositions because much of the microwave energy passes through the polymeric composition, i.e., the microwave energy is poorly absorbed by the polymeric compositions. Thus, heat from microwave energy will not be evenly distributed throughout the article and parts of the article heated with microwave energy may begin to degrade before the other portions of the article are heated.

25 Efforts to use microwave energy to heat compositions have had limited success. Attempts to use microwave energy to distribute heat evenly to compositions include U.S. Patents 5,188,256 to Nottingham, et al. and U.S. Patent No. 5,368,799 issued to Haas et al., which are incorporated herein by reference. These patents describe a hot melt apparatus where

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microwave absorbable particles are incorporated into a composition that absorbs microwave energy and converts to heat which melts a neighboring thermoplastic composition.

Additionally, U.S. Patent No. 5,446,270 discloses the use of ferromagnetic particles in amounts up to 10% of the total composition, that have been dispersed or positioned in a matrix to be heated by microwave energy in general microwave applications. U.S. Patent 5,317,045 issued to Clark, Jr. et. al., discloses the application of microwave energy to remotely heat a polymeric material to a selected temperature. Specifically, Clark describes the use of thermosetting polymers to form joints in composite structures like those found in graphite composite frames of state of the art aircraft. Although these patents describe the use of ferromagnetic properties to absorb microwave energy and subsequently heat a polymeric material, they have had limited use in curing compositions due to uneven distribution of particles and the difficulty in uniformly curing a composition. The Clark patent is limited in its disclosure and teachings to low amounts of particles, particles from iron-lignosulfonate and to certain types of polymers and applications.

It would be desirable to provide compositions which can uniformly and controllably heat and cure with microwave energy. Additionally, it would be desirable to provide a heating method that cures heat curable compositions faster and more uniformly than conventional heating techniques, reducing the cost and improving the safety of the curing process.

SUMMARY OF THE INVENTION

In one aspect of the present invention there is provided a composition which is controllably heatable and curable by a microwave energy. The compositions include at least one heat curable resin component; microwave absorbable particles present in an amount of about 10% by weight of the composition, and at least one curing agent for the heat curable resin component. The microwave absorbable particles are selected such that the Curie temperature of the particles is higher than the curing temperature of the heat curable resin component. Application of microwave energy to the composition results in the microwave particles absorbing the energy, and converting it to radiant heat energy which rapidly cures the heat curable resin component.

In another aspect of the present invention there is a method for controllably curing a composition. This method includes the steps of selecting appropriate microwave absorbable

particles having a desired Curie temperature; combining the microwave-absorbable particles with a heat curable resin component, which has a curing temperature lower than the Curie temperature and is substantially transparent to microwave energy and the particles are present in an amount of about 10% by weight of the composition; and applying a sufficient amount and wavelength of microwave energy to the heat curable resin component to achieve the desired heating temperature.

The use of microwave absorbable particles to cure the compositions permits formation of articles such as gaskets or seals in minutes rather than hours. Additionally, this method provides uniform and controllable curing throughout the thickness of the composition, achieving requisite seal strengths without a hot press. By heating only the composition with the microwavable absorbent particles, and not the surrounding environment, i.e., air and equipment, results in energy conservation and improved safety. In fact, microwave energy source may be located at a remote distance from a seal to be cured, which greatly simplifies the curing process.

DETAILED DESCRIPTION OF THE INVENTION

The curable resin component used in the present invention may be a functionalized monomer, polymer, and/or oligomer which, in the presence of a curing agent, cures. Examples of heat curable resins include acrylics, elastomeric synthetic rubbers, epoxies, polyesters, polyurethanes, polybutadienes, cyanate esters, bismoleimides, polyimides, phenolics, alkyls, amino resins, silicones, acrylic silicones, epoxy silicones and copolymers and combinations thereof. Other useful curable resin components further include elastomeric deformable materials such as urethane, silicone-acrylate, urethane-acrylate, co-polymers and combinations thereof. One particularly useful heat curable resin is silicone elastomers, such as those used to construct gaskets for automobiles. The curable composition may be in a liquid, film or putty-like form which cures when exposed to heat.

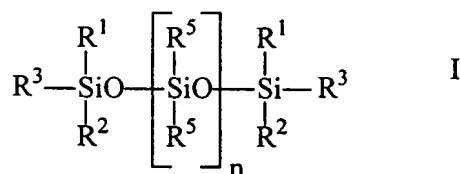
The heat curable resin component may be used in amounts of about 20% to about 95% by weight, and desirably about 40% to about 60% by weight of the total composition.

Useful curable resin components include, but are not limited to, linear or branched polyorganosiloxanes, polydimethylsiloxane chains having crosslinking sites located at either

the ends or the middle of the chains, cyclic siloxanes and combinations thereof. Radicals from thermal decomposition of peroxides crosslink polyorganosiloxanes with or without unsaturation. Saturated polyorganosiloxanes may result in a slower curing process than unsaturated polyorganosiloxanes. Particularly useful silicones include vinyl-terminated polysiloxanes. More particularly, dimethyl vinyl silyl terminated polydimethylsiloxanes (10,000 MW vinyl fluid and 62,000 MW vinyl fluid) have been found to be useful in the present invention as a heat curable resin component.

Polyorganosiloxanes having olefinic unsaturation should contain at least one reactive functional group, and desirably two reactive functional groups. More than two reactive functional groups are also advantageous in achieving certain cured properties. The number and type of functional group or groups present can be varied according to the desired properties of the final silicone composition. The organic groups of the polyorganosiloxane are monovalent hydrocarbon radicals and preferably the organo groups include alkyl radicals, such as methyl, ethyl, propyl, etc.; alkenyl radicals such as vinyl, allyl, etc.; cycloalkyl radicals such as cyclohexyl, cycloheptyl, and; mononuclear aryl radicals such as phenyl, ethylphenyl; and haloalkyl such as 3, 3, 3-trifluoropropyl.

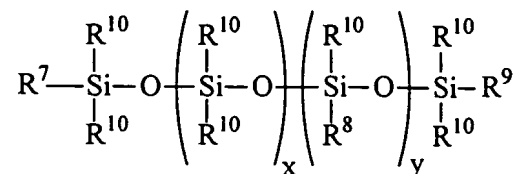
The polyorganosiloxanes of the present invention have the general formula:



wherein R^1 , R^2 , R^3 and R^5 can be the same or different and are substituted or unsubstituted hydrocarbon or hydrocarbonoxy radicals from C_{1-20} , provided that at least one of these R groups, and desirably more than one, include unsaturated functional groups which participate in heat curing, such as vinyl, (meth)acrylate, carboxylate, maleate, cinnamate and combinations thereof. For example, when one or more of the aforementioned R groups (R^1 , R^2 , R^3 and R^5) is not one of the required reactive functional groups, they can be chosen from alkyl radicals such as methyl, ethyl, propyl, butyl and pentyl; alkenyl radicals such as vinyl and allyl; cycloalkyl radicals such as cyclohexyl and cycloheptyl; aryl radicals such as phenyl, methylphenyl, ethylphenyl; arylalkyl radicals such as beta-phenylethyl; alkylaryl radicals; and hydrocarbonoxy radicals such as alkoxy, aryloxy, alkaryloxy, aryalkoxy, and desirable methoxy, ethoxy or hydroxy, and the like. Any of the foregoing radicals may have some or all of the hydrogen atoms replaced, for example, by a halogen such as fluorine or chlorine. One or more of the aforementioned R groups can also be hydrogen, provided the required reactive functional group is present as indicated and the presence of the hydrogen does not deleteriously interfere with the ability of the polyorganosiloxane to perform in the present invention. R^3 in the above formula desirably is a vinyl group or a dimethyl vinyl group.

The number of repeating units in the polyorganosiloxanes can be varied to achieve specific molecular weights, viscosities and other chemical or physical properties. Additional reactive polyorganosiloxanes are disclosed in U.S. Patent No. 5,212,211 to Welch II et al., which is incorporated by reference herein, may be used in the present invention. Generally n is an integer such that the viscosity is from about 25 cps to about 2,500,000 cps at 25°C, such as when n is from 1 to 1,200.

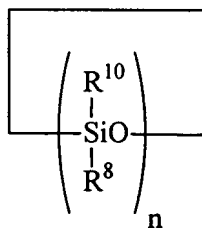
The silicon hydride crosslinker may be selected as the curing agent and conforms to the formula below:



wherein at least two of R⁷, R⁸ and R⁹ are H; otherwise R⁷, R⁸ and R⁹ can be the same or

5 different and can be a substituted or unsubstituted hydrocarbon radical from C₁₋₂₀ such hydrocarbon radicals including those as previously defined for formula I above; thus the SiH group may be terminal, pendent or both; R¹⁰ can be H and can also be a substituted or unsubstituted hydrocarbon radical from C₁₋₂₀ such hydrocarbon radicals including those as previously defined for formula I above, and desirably is an alkyl group such as methyl; x is an
10 integer from 10 to 1,000; and y is an integer from 1 to 20. Desirably, R groups which are not H are methyl. The silicon hydride crosslinker should be present in amounts sufficient to achieve the desired amount of crosslinking and desirably in amounts of about 1 to about 10% by weight of the composition.

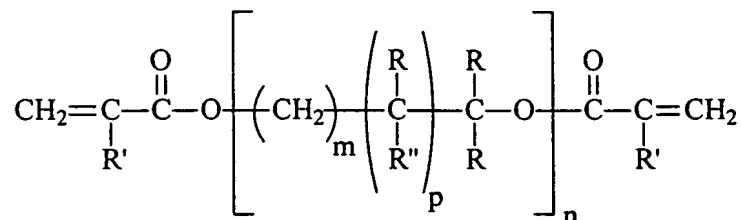
15 Other silicon hydride crosslinkers are also contemplated including those of the formula:



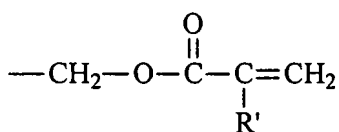
wherein R⁸ and R¹⁰ can be the same or different and can be H or a substituted or unsubstituted hydrocarbon radical from C₁₋₂₀ such hydrocarbon radicals including those as previously defined for formula I above and n is an integer from 3 to 30. R¹⁰ desirably is an alkyl group such as
20 methyl. Desirably, R groups which are not H are methyl.

Examples of useful (meth)acrylic compositions include, without limitations those described in U.S. Patent Nos. 3,043,820, 3,425,988, 4,103,081 and 4,262,106, all of which are

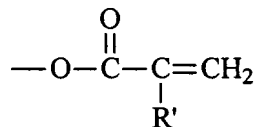
herein incorporated by reference. An example of (meth)acrylic compositions useful in the present invention are those which correspond to the following general structure:



- 5 wherein R represents a radical selected from the group consisting of hydrogen, lower alkyl of 1-4 carbon atoms, hydroxy alkyl of 1-4 carbon atoms, and



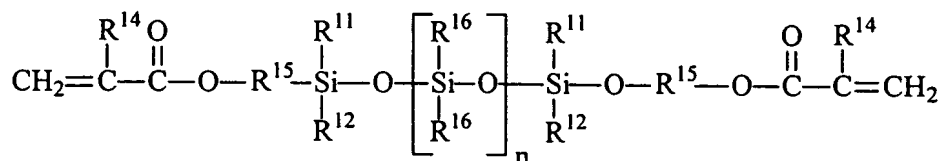
- 10 wherein R' is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of 1-4 carbon atoms; R'' is a radical selected from the group consisting of hydrogen, -OH and



- 15 wherein m is an integer equal to at least 1, e.g., from 1 to 8 or higher, and preferably from 1 to about 4; n is an integer equal to at least 1, for example, 1 to 20 or more; and p is 0 or 1.

Useful acrylic functional silicone compositions include for example, those disclosed in Loctite U.S. Patent Numbers 4,503,208, 4,528,081, 4,699,802 and 4,675,346, the disclosures of which are incorporated herein by reference. Among the acrylic silicone compositions disclosed therein are those which include compounds having the chemical formula:

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wherein n is an integer from about 50 to about 2000, R¹¹ may be H, alkyl, amino, oxime or -OOCR¹³; R¹² is R¹¹ or hydrocarbyl such as alkyl, aryl, substituted aryl, alkoxy, aryloxy or acrylic groups; R¹³ is hydrocarbyl, R¹⁴ is H or methyl, R¹⁵ is an organo group having a carbon atom bound to the adjacent silicon atom and R¹⁶ is a hydrocarbyl group, such as substituted alkyl, aryl or substituted aryl groups. Specific examples of R¹¹ and R¹² groups are alkyls, such as methyl and ethyl, halo groups such as trifluoropropyl, phenyl and benqyl. R¹¹ and R¹² may also include moisture curable groups such as methoxy. Desirably, R¹³ and R¹⁴ are methyl. More specifically, R¹⁵ may be alkylene, alkyleneoxy, alkenylene of 3-10 carbon atoms, such as propylene and propenylene or arylene groups. Such siloxane compounds may have molecular weights which vary, but desirably are at least about 1,000.

When silicone compositions are employed in the heat curable resin component of the present invention, these compositions may employ hydrosilation addition chemistry to cure. Hydrosilation addition cure is a catalyzed heat cure reaction which uses the presence of one or more unsaturated groups in the heat curable silicone resin component. Examples of heat curable silicone resin components include, but are not limited to polyorganosiloxane containing ethylenically unsaturated functionalities and monomeric silanes containing ethylenically unsaturated functionalities. For example, vinyl terminated polydimethylsiloxane, tetramethyl tetravinyl cyclotetrasilane or tetrakis(vinyl dimtheysilyl)silane may be employed.

When heat curable silicone resins are employed in the present invention, a hydrosilation cross-linker are employed along with a hydrosilation catalyst. Hydrosilation cross-linkers include, but are not limited to, linear polyorganosiloxanes, monomeric silanes,

polydimethylsiloxane chains having SiH functionality located at either the ends or the middle of the chains and cyclic siloxanes. Desirably, the first silicon containing material is selected from the group consisting of SiH terminated polydimethylsiloxane, copolymers of polydimethyl siloxane and polymonomethyl siloxane, tetrakisdimethylsilylsilane, and tetramethyl cyclotetrasiloxane.

The polymerizable polyacrylate esters utilized in accordance with the invention and corresponding to the above general formula are exemplified by, but not restricted to, the following materials: di-, tri- and tetrathyleneglycol dimethacrylate; dipropyleneglycol dimethacrylate; polyethyleneglycol dimethacrylate; di-(pentamethyleneglycol) dimethacrylate; tetraethyleneglycol diacrylate; tetraethyleneglycol di(chloroacrylate); diglycerol diacrylate; diglycerol tetramethacrylate; tetramethylene dimethacrylate; ethylene dimethacrylate; neopentylglycol diacrylate; and trimethylolpropane triacrylate.

While di- and other polyacrylate esters have been found particularly desirable, monofunctional acrylate esters (esters containing one acrylate group) also may be used, such as those having a relatively polar alcoholic moiety. Such materials are less volatile than low molecular weight alkyl esters and, more important, the polar group tends to provide intermolecular attraction in the cured polymer, thus producing a more durable sealant or adhesive. Desirably, the polar group is selected from labile hydrogen, heterocyclic ring, hydroxy, amino, cyano, and halogen polar groups, more specific examples of which are cyclohexylmethacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, cyanoethylacrylate, and chloroethyl methacrylate.

Curable polyolefinic monomers may be used as the heat curable resin component, including acrylic and methacrylic resins, vinyl monomers, unsaturated polyesters solubilized in vinyl monomers and mixtures thereof. Particularly useful curable resin components are ethoxylated trimethylolpropane triacrylate, trimethylol propane trimethacrylate, dipentaerythritol monohydroxypentacrylate, pentaerythritol triacrylate, ethoxylated trimethylolpropane triacrylate, 1,6-hexanedioldiacrylate, neopentyl glycoldiacrylate, pentaerythritol tetraacrylate, 1,2-butylene glycoldiacrylate, trimethylolpropane ethoxylate tri(meth)acrylate, glyceryl propoxylate tri(meth)acrylate, trimethylolpropane tri(meth)acrylate,

dipentaerythritol monohydroxy penta(meth)acrylate, tri(propylene glycol) di(meth)acrylate, neopentylglycol propoxylate di(meth)acrylate, 1,4-butanediol di(meth)acrylate, polyethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, butylene glycol di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate and combinations thereof.

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Epoxy resins useful in the compositions of the present invention include polyepoxides curable by elevated temperature. Examples of these polyepoxides include polyglycidyl and poly(β -methylglycidyl) ethers obtainable by reaction of a compound containing at least two free alcoholic hydroxyl and/or phenolic hydroxyl groups per molecule with the appropriate epichlorohydrin under alkaline conditions or, alternatively, in the presence of an acidic catalyst and subsequent treatment with alkali. These ethers may be made from acyclic alcohols such as ethylene glycol, diethylene glycol, and higher poly(oxyethylene) glycols, propane-1,2-diol and poly(oxypropylene) glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol, and poly(epichlorohydrin); from cycloaliphatic alcohols such as resorcinol, quinitol, bis(4-hydroxycyclohexyl)methane, 2,2-bis(4-hydroxycyclohexyl)propane, and 1,1-bis(hydroxymethyl)-cyclohex-3-ene; and from alcohols having aromatic nuclei, such as N,N-bis(2-hydroxyethyl)aniline and p,p'-bis(2-hydroxyethylamino)diphenylmethane. Or they may be made from mononuclear phenols, such as resorcinol and hydroquinone, and from polynuclear phenols, such as bis(4-hydroxyphenyl)methane, 4,4'-dihydroxydiphenyl, bis(4-hydroxyphenyl) sulphone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2,-bis(4-hydroxyphenyl)propane (otherwise known as bisphenol A), 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, and novolaks formed from aldehydes such as formaldehyde, acetaldehyde, chloral, and furfuraldehyde, with phenols such as phenol itself, and phenols substituted in the ring by chlorine atoms or by alkyl groups each containing up to nine carbon atoms, such as 4-chlorophenol, 2-methylphenol, and 4-t-butylphenol.

Poly(N-glycidyl) compounds include, for example, those obtained by dehydrochlorination of the reaction products of epichlorohydrin with amines containing at least two amino-hydrogen atoms, such as aniline, n-butylamine, bis(4-aminophenyl)methane, and bis(4-methylaminophenyl)methane; triglycidyl isocyanurate; and N,N'-diglycidyl derivatives of cyclic alkylene ureas, such as ethyleneurea and 1,3-propyleneureas, and of hydantoins such as 5,5-dimethylhydantoin.

Epoxide resins having the 1,2-epoxide groups attached to different kinds of hetero atoms may be employed, e.g., the N,N,O-triglycidyl derivative of 4-aminophenol, the glycidyl ether-glycidyl ester of salicylic acid, N-glycidyl-N'-(2-glycidyloxypropyl)-5,5-dimethylhydantoin, and 2-glycidyloxy-1,3-bis(5,5-dimethyl-1-glycidylhydantoin-3-yl)propane.

Such epoxies are available from a variety of commercial sources, such as the EPON series from Shell Chemical Co., the EPI-REZ series from Rhône-Poulenc, the Araldite series from Ciba-Geigy, the D.E.R. series from Dow Chemical Co., and the EPOTUF series from Reichhold.

Also useful are halogenated epoxy resins such as the brominated epoxides available from the sources shown above. Halogenated epoxy resins in combination with other fire retardant materials may be suitable for use as fire retardant additives in the compositions of the present invention.

Especially preferred epoxy resins useful in the present invention are the diglycidyl ethers of bisphenol A marketed under the tradenames EPON 825 and EPON 828 available from Shell Chemical Co., D.E.R. 331 and 332 available from Dow Chemical Co., and the cycloaliphatic epoxy resin marketed as ERL-4221 by Union Carbide Co.

Various epoxies such as the glycidyl ethers marketed as the EPODIL series by Pacific Anchor Chemical Corporation, a division of Air Products and Chemicals Inc., may be added as epoxy diluents, to reduce the viscosities of the resins of the present invention.

The type of curing agent is chosen based on the choice of heat curable resin component. A curing agent is generally employed to initiate or otherwise promote the curing of the polymer or monomer. Useful curing agents include an amine-containing compound, an azo compound and a peroxide curing agent. In the case of (meth)acrylic compositions, peroxy initiators are generally employed. In the case of heat curing silicone compositions, platinum compositions are often employed.

Curing agents commonly employed in the present compositions are often included in an amount less than about 20% by weight of the composition. Desirably, they are employed in lower levels such as 0.025% to about 10%, desirably about 1 to about 5% by weight of the total composition.

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Peroxy initiators useful in (meth)acrylic compositions include the hydroperoxy curing agents and most preferably the organic curing agents having the formula ROOH , wherein R generally is the hydrocarbon radical containing up to about 18 carbons, desirably an alkyl, aryl or aralkyl radical containing up to about 12 carbon atoms. When warmed to a specific temperature, peroxide curing agents decompose exothermically into free radicals with a half-life period which is characteristic for each peroxide. In the presence of polymerizable double bonds, these free radicals add themselves on thereto and initiate the polymerization.

Typical examples of such hydroperoxides include cumene hydroperoxide, methylethylketone hydroperoxide, para-menthane hydroperoxide, tertiary butyl hydroperoxide as well as hydroperoxides formed by the oxygenation of various other hydrocarbons such as methylbutene, cetane and cyclohexane. Other peroxy initiators such as hydrogen peroxide or materials such as organic peroxides or peresters which hydrolyze or decompose to form hydroperoxides such as tertiary butyl perbenzoate may also be employed. Organic peroxides, for example percarbonates, diacyl peroxides, per-esters, per-acids or ketone hydroperoxides, are used to a great extent as initiators for free-radical polymerization.

Other known initiators of free radical polymerization such as saccharin and a variety of secondary and tertiary organic amines are useful in the inventive compositions. A common combination of these initiators involves a hydroperoxide, saccharin and aromatic amine system. The use of metal catalysts, alone or in combination with other conventional accelerators are also useful.

Various conventional heat-activated curing agents for epoxies are useful in the present invention including imidazoles, preferably 2-ethyl-4-methyl imidazole, 1-(2-cyanomethyl)-2-ethyl- α -4-methylimidazole and 2-phenyl-4,5-dihydroxymethyl imidazole; aliphatic cycloaliphatic amines, preferably 2,2'-dimethyl-4,4'-methylene-bis(cyclohexylamine) (Ancamine 2049); aromatic amines, preferably 4,4'-diaminodiphenyl sulfone (Ancamine S and

Ancamine SP); a blend of aromatic and aliphatic amines (Ancamine 2038); Lewis Acid catalysts such as boron trifluoride:amine complexes, preferably BF₃:benzyl amine (Anchor 1907), BF₃:monoethyl amine (Anchor 1948) and liquid BF₃:amine complex (Anchor 1222); Lewis Base catalysts such as t-amines, preferably tris(dimethyl-aminomethyl)phenol (Ancamine K.54), dimethylaminomethyl phenol (Ancamine 1110); dicyandiamides, preferably dicyandiamide (Amicure CG). The Ancamine, Anchor, and Amicure series are tradenames for heat activated curing agents marketed by Pacific Anchor Performance Chemicals Division of Air Products and Chemicals, Inc.

Especially pertinent to the anhydride resin compositions of the present invention are the acid anhydride epoxy curing agents. These include, preferably, methyltetrahydrophthalic anhydride, methylhexahydrophthalic anhydride, chlorendic anhydride, and nadic methyl anhydride and mixtures thereof. Nadic methyl anhydride is available as AC-methyl from Anhydrides and Chemicals, Inc.

It will be noted that anhydride based catalysis of epoxy polymerization is an inherently slow process. Accordingly, the resin compositions of the present invention generally employ a minor amount of amine accelerators of the anhydride catalysis, preferably benzyl dimethylamine; 2-ethyl-4-methyl imidazole, available as Imicure EMI-24 from Pacific Anchor; and 2,4-diamino-6[2'-methylimidazolyl-(1)]ethyl-s-triazine isocyanurate adduct.

Accelerators may be used to affect the cured properties of the compositions in areas of adhesion and sensitivity to oxygen and to speed curing of the composition. Amines and organic sulfimides are examples of useful accelerators. Among the useful amines include amine oxides, sulfonamides and triazines. The use of accelerators may be in amounts of about 0.1 to about 5, preferably about 1 to about 2, percent by weight of the total composition.

Catalysts may be added to the curable composition to help promote curing. A platinum catalyst is useful for addition curing systems. The platinum catalyst may be solid platinum, deposited on a carrier such as charcoal or gammaalumina. Any type of platinum catalyst compatible with the present invention may be used. The catalyst may be utilized in the amounts from about 0.02% to about 20% of the total composition.

It is generally desirable that the catalyst is a solubilized platinum catalyst complex. Useful catalyst and curing agent solutions include methyl hydrogen polysiloxane solution with a 25% platinum catalyst solution, cyclo tri(vinyl methylsiloxane) with a $\text{Pt}(\text{CO})_2\text{Cl}_2$ solution and combinations thereof in amounts of 0.02-20.0% and desirably 0.02-5.0% by weight of the solution.

Other classes of catalysts include, in addition to organoplatinum and organoplatinum complexes, organorhodium and platinum alcoholates. Complexes of ruthenium palladium, osmium and iridium are also contemplated. Organoplatinum catalysts are particularly useful herein. Of the non-platinum based catalysts useful, those based on rhodium are most preferred. The organometallic hydrosilation catalysts may be used in any effective amount to effectuate thermal curing. Combinations of various precious metal or precious metal-containing catalysts are contemplated. The amount of this catalyst is not critical so long as proper crosslinking is achieved.

Other agents such as viscosity modifiers, plasticizers, fillers, and other well-known additives may be incorporated where functionally desirable. For example, chelating agents may also be employed to sequester any metal contaminants present in the composition which would contribute to spurious curing prior to intended use.

According to the methods of the present invention, the microwave absorbable particles provide uniform heating and curing of microwave curable compositions that are otherwise substantially transparent to or non-absorbent of microwave energy. With the inventive methods, the temperature of the composition increases to and is maintained at a temperature, the Curie temperature of the particles, which is desirably a temperature sufficient to heat and cure but not degrade the composition, even when additional microwave energy is added to the composition. The unique nature of this method is superior over conventional heating techniques in that it is not only faster, but provides for a uniform heating and curing of thin or thick compositions without degrading any part of the compositions.

Useful microwave absorbable particles include ferromagnetic compounds, metal oxides, in general, ferrites, amorphous carbon containing compounds such as carbon black and graphite, and other materials which readily absorb microwave energy of the desired frequency.

Useful ferromagnetic compound particles include ferrites with spinel structure, hexagonal structure and nonlinear structure. Particularly useful ferromagnetic particles are spinel ferrites with the general formula of $M^{2+} Fe_2^{3+} O_4$, where M^{2+} is a divalent metal ion. Ferrite particles are especially useful for their inherent temperature limiting capabilities. The amorphous carbon compounds are preferred for their ability to produce controllable heating. Particles desirable have diameters from about 50 to about 1000 Angstroms and Curie temperature ranges from about 50°C to about 700°C. The microwave absorbable particles may be present in any amount to achieve the desired heating or curing effect. More specifically, the microwave absorbable particles are present in amounts of at least 10% by weight of the composition, and desirably about 10% to about 40% by weight of the total composition.

In the present invention, attention is given to the selection of microwave absorbable particles. The microwave absorbable particles are chosen for the frequency at which it absorbs radiation and for its Curie temperature. The Curie temperature is the temperature at which a material can no longer absorb microwave energy through its magnetic properties. The Curie temperature of the microwave absorbable particles is chosen so that it has the desired effect upon the curable resin component within which it is embedded. The microwave absorbable particles selected for use in the present invention may be chosen so that their Curie temperature is just above the fusion temperature of the curable resin component thereby allowing for the source of microwave energy of the system to be selectively used to cure the composition. The microwave absorbable particles are selected such that reaching their Curie temperature would not degrade the composition or otherwise deleteriously affect the desired properties of the cured composition.

When a magnetic particle reaches or exceeds a critical temperature, referred to as the Curie temperature, its magnetic permeability drops precipitously to a value approaching 1. The particle then loses much of its ability to respond to a magnetic field and heating is significantly diminished. When the temperature of the particle drops below the Curie point, the particle regains its magnetic properties and heating resumes. Therefore, when the temperature of the particle is less than the Curie temperature, the particle heats. When the temperature of the particle is greater than the Curie temperature, the particle essentially stops increasing in

temperature. Thus, the Curie point is a practical autoregulation means for preventing the host material from being overheated.

In contrast to the prior art, the present invention finds that curable compositions
5 containing high amounts of microwave absorbable particle, are not only practicable but also work well. For example, as evidenced in the examples, compositions containing microwave absorbable particles in an amount up to 40% by weight of the total composition cured extremely well.

10 Heat is generated throughout the region containing the microwave absorbable particles, permitting far greater control over the heating and curing of the compositions. Dispersing the particles evenly throughout the bulk of the composition facilitates uniform heating. Placement of the microwave absorbable particles, and the direction of microwave energy can be used to isolate the location of heat generation and curing. Thus, selective heating will result where the
15 particles are placed in higher concentrations in areas to be heated to a relatively greater extent. In either case, the temperature of articles loaded with the microwave absorbable particles is controllable by utilization of particles having a Curie temperature near the desired temperature.

It is contemplated that other frequencies outside the microwave range could be used so
20 long as it is able to cure the composition. For example, frequencies found in the radio frequency range, as are commonly known, are also useful. Useful frequencies include frequencies from about 10 KHz to about 100 GHz. Microwaves in the upper section of the frequency range are preferred due to the fact that they are easier to direct into a relatively narrow beam. The ability to collimate in focus such microwave energy is a particularly useful
25 feature in the context of this invention, as it allows the system operators to deliberately and remotely apply microwave energy to a particular location where it is desirable to heat the composition.

Other agents that may be added to the curable composition of the present invention
30 include catalysts, inhibitors, viscosity modifying agents, coloring agents, fluorescent agents and combinations thereof. Other agents may be used in an amount that imports the desired effect onto the composition and in particular in amounts from about 0.1% to about 40% by weight. Viscosity modifying agents may be used to desirably alter the viscosity of the uncured

composition. Particularly useful viscosity modifying agents include fumed silica, precipitated silica, water and combinations thereof. The silica may be either treated with cyclic polysiloxane, silazanes and combinations thereof. Useful viscosity modifying agents further include titanium dioxide, lithopone, zinc oxide, zirconium silicate, silica aerogel, iron oxide, diatomaceous earth, calcium carbonate, silazane treated silicas, glass fibers, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, alpha quartz, calcined clay, carbon, graphite, cork, cotton, synthetic fibers, solid acetylinic acid and the like.

Stabilizers and inhibitors may also be employed to control and prevent premature peroxide decomposition and polymerization. Inhibitors and stabilizers incorporated into curing systems will prevent the compositions from curing at room temperature but won't prevent curing at elevated temperatures. Among those useful inhibitors include phenols such as hydroquinone and quinones as well as those selected from the class consisting of vinyl containing organocyclo tetrasiloxanes such as a methyl vinyl cyclotetrasiloxane, trialkylcyanurate, alkyl maleates and combinations thereof. Particularly useful inhibitors include hexamethyldisilazane (HMDS), amines, α -hydroxyacetylene and combinations thereof. The solvents methanol and ethanol and mixtures thereof may also be used as an inhibitor to suppress the reaction between curable component and the curing agents contained for almost indefinite periods at room temperature.

There are many applications where the methods and compositions of the present invention are useful. The present invention may be used for any application where microwave energy is used as the heating source. For example, the inventive curable compositions and the inventive curing methods work well for manufacturing basic materials such as gaskets and other preformed sealant devices.

The methods of the present invention permit formation of seals in a position remote to the source of the microwave energy. The inclusion of the microwave absorbable particles in a curable composition permits remote inspection of the seal. For example, in the application of the invention, a quantity of microwave absorbable particles is intermixed with the heat curable resin component that is in a putty-like form that is a flowable adhesive paste. This composition is applied between the surfaces to be bonded together. Then, the curable composition may be exposed to a collimated beam of microwaves radiated from the source of microwave radiation.

Such a beam may be easily and conveniently applied even when the curable composition is disposed behind a panel, so long as the panel is transparent to microwave radiation. The absorption of the beam of microwave energy by the microwave absorbable particles within the composition causes the curable composition to heat up to the Curie temperature of the ferromagnetic material and to cure the composition.

Additionally, the directability of the beam of microwaves from the microwave source, coupled with the fact that these microwaves easily penetrate through most non-metallic components, confers great utility of this particular embodiment of the system in creating joints or in repairing joints in compositions structures with microwave absorbable particles. Compositions and methods of the present invention allow joints and seals to be created without the application of unwanted heat to large portions of the composite structure being built, and further allows such heat to be selectively and remotely applied to portions of the resulting structure which are either physically inaccessible to the microwave source, or covered by microwave-transparent components such as panel.

When used as a bonding material, it may be useful for the inventive compositions to be in form of a tape that includes an adhesive on at least one side for affixing it to one side of the surface prior to the application of the microwave energy. The tape form of the inventive compositions can be used in the methods of the present invention.

EXAMPLES

Various compositions were prepared and tested for their suitability as a microwave curable composition. These compositions, as shown in Table 1 were prepared by combining the respective components as shown in table and uniformly mixing them together to form the compositions. Compositions typically included the curable resin component, microwave absorbable particles, curing agent, catalyst solution, inhibitors and viscosity modifiers. The amount of microwave absorbable particles ranged from about 6% to about 40% by weight. The test samples were prepared by placing the uncured inventive compositions onto a 3" long and 1/2-3/4 diameter Ultem® slab. Ultem® (from General Electric, Fairfield, CT) is a polyetherimide plastic chosen for its microwave transparency and resistance to heat.

TABLE 1
INVENTIVE COMPOSITIONS (WEIGHT % OF TOTAL COMPOSITION)

Component	Composition 1	Composition 2	Composition 3	Composition 4	Composition 5	Composition 6
Heat Curable Resin Component						
Poly dimethylsiloxane-vinyl terminated (62,000 MW Vinyl Fluid)	29.22	29.07	26.57	32.28	25.56	20.62
Poly dimethylsiloxane, dimethyl, vinyl terminated (10,00 MW Vinyl Fluid)	32.83	32.67	27.31	33.18	27.30	21.20
Microwave Absorbable Particles						
Ferrite Particles ¹	15.00	14.93	22.74	6.08	22.73	40.00
Catalyst/Curing Agent						
Methyl hydrogen polysiloxane (25% pt catalyst solution)	2.70	3.2	3.00	3.65	3.00	2.33
Cyclo tri(vinyl methylsiloxane) + Pt (CO) ₂ Cl ₂	0.05	0.05	0.025	0.06	0.05	0.038
Inhibitors						
Hexamethyldisilazane (HMDS)			1.82	2.21	1.82	1.41
2-Phenyl-3-butyl-2-ol			0.18	0.22	0.18	0.14
Viscosity Modifiers						
Water			0.18	0.22	0.18	0.14
Silica	20.00	19.90	18.18	22.10	18.18	14.12
Solid acetylinic alcohol	0.2	0.2				

¹Manganese zinc ferrite (Steward Co.)

The ability of the compositions to cure over a period of time was observed and recorded in Table 2 and 3. The percent cured was measured by determining the amount of paste (uncured) versus the amount of solid material (cured). Also recorded in Table 2 and 3 is the hardness level of the composition as measured on the Shore Hardness scale. Table 3 describes curing speed and hardness of inventive compositions 4, 5 and 6 using the heat press curing method at 150°C and Table 2 describes curing speed and hardness of the inventive compositions cured using microwave energy. As shown in Table 2, inventive composition 6 with 40% microwave absorbing particles by weight of the total composition cured using microwave energy in less than 1 minute. Inventive composition 5, which had 22% by weight microwave absorbable particles, cured within 2 minutes and inventive composition 4, which has 6% by weight microwave absorbable particles, cured within 5 minutes. In contrast, as shown in Table 3, the inventive compositions 4,5 and 6 all cured at about 15 minutes using a heat press curing method at 150°C. Thus, curing times using microwave energy method are substantially faster than the curing times using the heat press curing method.

Additionally, Table 2 and 3 show that the curing process using heat press cure was less uniform than the microwave energy curing process. The inventive compositions cure more rapidly and uniformly with the microwave energy curing method than with the conventional curing methods.

The hardness values, as shown in Table 2 and 3, of the cured compositions using either curing method are all approximately equivalent. Thus, the amount of microwave absorbable particles does not adversely affect the hardness of the cured composition.

TABLE 2
Compositions Cured With Microwave Energy (High Energy)

Microwave Curing Time	Composition 4 (6% ferrite)		Composition 5 (22% ferrite)		Composition 6 (40% ferrite)	
	Observed Level of Cure	Hardness Shore A	Observed Level of Cure	Hardness Shore A	Observed Level of Cure	Hardness Shore A
1 min.	no cure	NA	Partially cured (surface/interior cured	NA	100% cure	40
2 min.	no cure	NA	no cure at interface)	33	100% cure	40
4 min.	Partially cured (interface at edges uncured)	42	100% cure	35	100% cure	
5 min.		42	100% cure	36	100% cure	
6 min.	100% cure	--	100% cure	38	100% cure	
8 min.	100% cure	40	100% cure	37	100% cure	
10 min.	100% cure	--	100% cure	37	100% cure	
12 min.	100% cure	40	100% cure	38	100% cure	
15 min.	100% cure	41	100% cure	38	100% cure	

TABLE 3
Compositions Cured With Heat Press Cure at 150° C

Curing Time	Composition 4 (6% ferrite)		Composition 5 (22% ferrite)		Composition 6 (40% ferrite)	
	Observed Level of Cure	Hardness Shore A	Observed Level of Cure	Hardness Shore A	Observed Level of Cure	Hardness Shore A
2 min.	no cure	NA	no cure	NA	no cure	NA
4 min.	no cure	NA	no cure	NA	no cure	NA
5 min.	no cure	NA	no cure	NA	no cure	NA
6 min.	partially cured (interior interfaced not cured)	NA	partially cured (interior & interface not cured)	NA	no cure	NA
8 min.	partially cured (interior & interface not cured)	NA	partially cured (interior & interface not cured)	NA	partially cured (interior & interface not cured)	NA
10 min.	partially cured (edges cured interior at center is soft)	NA	partially cured (edges cured, interior at center is soft)	NA	partially cured (edges cured, interior at center is soft)	NA
12 min.	partially cured (large central portion at interface uncured)	42	partially cured (small central portion at interface uncured)	42	partially cured (interior is soft)	NA
15 min.	cured	45	cured	48	cured (with some difficulty removing material)	50
20 min.	cured	47	cured	47	cured	47

Table 4, 5 and 6 compare the physical properties of the cured inventive composition 1, 2 and 3 produced by microwave energy and heat press curing methods. Compositions 1 and 2 have levels of microwave absorbable particles of about 15%, as shown in Table 1. It is evident from Table 4 and 5 that the microwave cured composition 1 and 2 have physical properties that are similar to those of the heat press cured composition 1 and 2. Upon further curing, the properties of the heat press cured compositions did not substantially change except for the elongation values and the compression set values decreased slightly. In contrast, the properties of the microwave cured compositions stayed substantially the same when they were further cured. Thus, further microwave curing of the inventive compositions does not enhance or degrade the physical properties of the inventive compositions.

As seen in Table 6, inventive composition 3 was microwave cured for 3.5 minutes followed with by a post cure by a heat press method for 16 hours at 150°C. The results from this table exemplify that further heat press curing of inventive composition 3 that was originally microwave cured does not substantially enhance or degrade the physical properties of the inventive composition. The post cured composition does show a slight increase in hardness, tensile strength, 50% modulus and fracture point, while a slight decrease was observed in the compression set and percent elongation values.

TABLE 4**Heat Curable Compositions Cured Using Conventional Heating Methods (Heat Press)**

	Composition 1		Composition 2	
	Heat Press Cure 1 hr. at 120°C. and 30 min. at 150°C.		Heat Press Cure 1 hr. at 120°C. and 30 min. at 150°C.	
	No Post Cure	Post Cured an Additional 18 hrs. at 150°C.	No Post Cure	Post Cured an Additional 18 hrs. at 150°C.
Hardness Shore A	43	44	51	51
Tensile Strength (psi)	419	490	449	481
50% Modulus (psi)	206	277	242	350
100% Modulus (psi)	347	340	392	--
% Elongation	130	110	116	79
Compression Set (% Original Deflection)	65	36	37	36

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TABLE 5
Heat Curable Compositions Cured Using the Inventive Curing Method
(Microwave Energy)

	Composition 1		Composition 2	
	Microwaved Cured for 5 minutes at High Temperature		Microwaved Cured for 5 minutes at High Temperature	
	No Post Cure	Post Cured for 5 Minutes at High Temperature	No Post Cure	Post Cured in Microwave for 5 Minutes
Hardness Shore A	42	43	45	51
Tensile Strength (psi)	354	457	404	374
50% Modulus (psi)	146	186	178	220
100% Modulus (psi)	277	352	343	--
% Elongation	133	134	121	88
Compression Set (% Original Deflection)	59	60	46	45

TABLE 6
Microwave Cured/Post Heat Press Cured Composition

	Microwave cured for 3.5 min.	
	No post cure	Post cured by Heat Press for 16 hours at 150°C
Hardness Shore A	43	50
Tensile Strength (psi)	649	676
50% Modulus (psi)	251	306
100% Modulus (psi)	464	--
% Elongation	154	118
Compression Set (% Original Deflection)	42	30
Approx. Fracture Point (inch lbs.) (Sample thicknesses = 0.1"	76	83

From these examples it is evident that the inclusion of the microwave absorbing particles provides compositions that can be heated and cured by microwave energy with extraordinary control, yielding uniformly cured articles with faster curing times. The increased control over the application of heat to the composition will increase safety, reduce loss of heat to the surrounding environment and reduce manufacturing costs.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all modifications are intended to be included within the scope of the following claims.